Heat Transferred by Decomposition Products from Cotton Fabrics Exposed to Intense Thermal Radiation

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Abstract

Heat is transferred to skin protected against intense thermal radiation by several mechanisms. Textile fabrics provide considerable protection but some of them tend to decompose, producing tars which condense on the skin. The amount of energy transferred by tars from cotton fabrics was estimated by determining the amount of tar deposited and the amount of energy required to re-evaporate the tar. Two fabrics were used; one untreated, the other fire resistant treated (FR) with brominated triallyl phosphate. The energy amounts to about 500 cal for each gram of tar evaporated and is about the same for the two fabrics. Over the range of interest, the amount of tar deposited increased with increase in exposure. For fabric in contact with a skin simulant, the energy transferred by this mechanism varied up to 1 cal cm^{-2} of fabric; for the spaced arrangement, up to 1.5 to 2 cal cm^{-2}. For low and intermediate exposures, the energies transferred by the tar were about the same for the two fabrics; at the highest exposures, the values were considerably greater for the FR treated fabric. At exposures which produce disabling burns, the heat transferred by the tars is negligible for fabric in contact with the skin but for fabrics spaced from the skin, the tars may account for a fourth or more of the total energy transferred. Without this energy, the burn would be greatly reduced.

Introduction

Protected skin exposed to intense thermal radiation will be burned if sufficient energy is transferred to it rapidly. A schematic representation of exposure conditions is shown in Figure 1. The process is complicated, even with inert protective materials. Some of the incident radiation may be transferred through the protection and part way through the skin; some of the energy will be absorbed in the

protective layer, raising its temperature, and some of this heat will be transferred to the skin by various processes, including conduction, convection and radiation. All of these processes will depend on the surface temperatures of cloth and skin and the first two will depend on the degree of contact between cloth and skin.

If the protective system is not inert, which is the usual case with textile fabrics, the process is more complicated. Most fabrics contain appreciable amounts of moisture which may evaporate and con-
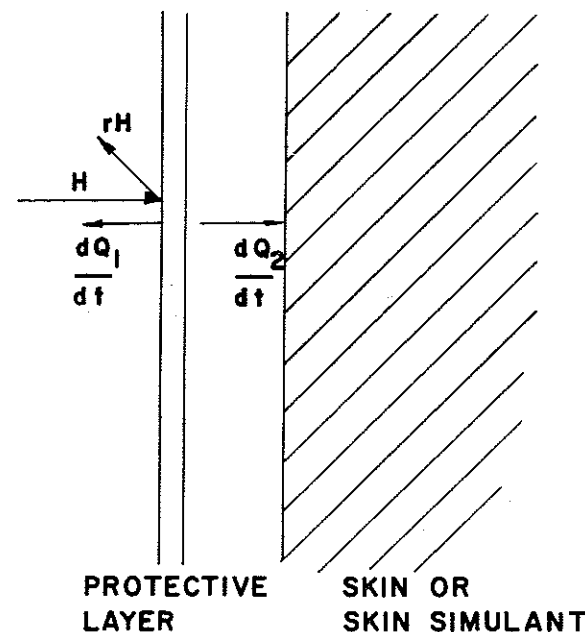
Fig. 1. Schematic representation of exposure arrangement.

dense on the skin, transferring an appreciable amount of energy. Of more significance, exothermic processes may occur in the fabric, changing its temperature and influencing all subsequent processes. In addition, at the exposures to which textile materials are subjected for practical protection, cotton fabrics, in particular, may decompose. Volatile decomposition products will then condense on the skin in the form of tars and transfer considerable amounts of heat. Such tars are readily apparent on both inanimate receivers and skin protected by cotton cloth. Pacsu, Schwenker and Way [21] have determined the chemical composition of tars collected from fabrics degraded at high temperature. For unmodified cotton they found the following percentages: water, 55; levo glucosan, 12.5; carbonyl compounds, including formaldehyde and glyoxal, ~15; acid compounds, ~7.5; unknown compounds, 10.

It is desirable to determine quantitatively the part played by each of these heat-transfer processes in producing skin burns, but up to now it has not been possible to separate effectively the several effects. It is difficult to measure directly or to calculate the amounts of heat transferred by the various processes. Since the amount carried by mass transfer of decomposition products seemed to be significant, an attempt was made to measure this indirectly by essentially studying the process in reverse. The heat required to re-evaporate the tars can be measured under condi-

tions approximating those existing during condensation. In a reversible process, this total quantity of heat to re-evaporate the tar should be exactly equivalent to the heat delivered to the skin by condensation but it is unlikely that the situation is this simple. Even with complications, a study of cotton fabrics provided useful information.

General Procedure

The problem was approached then by 1) determining the amount of tar deposited on a surface behind fabric under typical conditions of exposure, and 2) calculating the heat delivered by this amount of tar, assuming it was produced as a vapor and that on condensing on the backing surface, it gave up its heat of vaporization and additional heat by cooling to the final backing temperature. This required a measurement of the enthalpy changes experienced by the tars under these conditions.

Materials

Two fabrics were used. One was cotton sateen, 9 oz yd^{-2}, dyed OG-107, untreated, QM-3 of the Quartermaster standard fabric series [13]. The other was a similar fabric, treated with brominated triallyl phosphate (BTAP) for fire resistance, the add-on being about 19 percent. The first will be referred to as the untreated fabric; the second as the FR treated fabric.

Radiation

The source of radiation was the Natick Laboratories high-current carbon arc [15]. The radiation is somewhat similar to that of a black body at 6000° K, but with additional intense bands near .4 μ, presumably from cyanogen [12]. The flux distribution is of some importance in this experiment. Measurements by McQue [3] show that the irradiance is nearly uniform over a $\frac{1}{4}$-in. diameter, down 6 percent at a diameter of $\frac{3}{8}$ in., 16 percent at $\frac{5}{8}$ in. and 25 percent at $\frac{3}{4}$ in. The radiation was in the form of short pulses or steady flux as indicated later for each use.

Amount of Tar Condensed in Typical Exposures

The fabric was mounted, as a single layer, on a 4 in. × 4 in. × 1 in. thick transite block, either in contact or spaced $\frac{1}{4}$ in. from the block. In front of the fabric and in contact with it, was a Pyrex plate with a $\frac{3}{4}$-in. diameter aperture. Behind the fabric and in contact with the face of the transite block was an

aluminum foil, 2 in. square, 0.0006 in. thick, weighing about 0.1 g, which acted as the receiver of the tar.

Each sample was exposed to a 1-sec rectangular pulse of radiation, with exposures Q ranging from 5 to 15 cal cm^{-2}. After exposure and deposition of the tar, the foil was folded and placed in a closed bottle for weighing. Generally, the procedure was to expose a sample with the foil behind it and repeat the procedure using a new foil for each sample until tar from 5 fabric samples was collected. These were weighed together and the average amount of tar deposited by one exposure calculated from the total.

The tar from the $\frac{3}{4}$-in.-diameter exposed area was spread over a considerably greater area of the foil receiver. No attempt was made to measure the distribution on the foil and the amount collected was expressed in terms of unit area of exposed fabric, without attempting to take into account the deviations from uniform exposure within the exposed area.

The amounts of tar deposited for various exposures of the two fabrics and the two methods of exposure are given in Figure 2. This was the net amount collected and certainly not the total amount produced. Some of the vaporized material traveled away from the face of the sample and condensed elsewhere. The exact fate of the rest of it is uncertain. Some of it may have been trapped in the fabric. Some may have condensed in the space between fabric and backing and part of it deposited on the fabric, part on the backing, and part elsewhere. In any case, the amount collected on the backing determines the heat transferred to it, which is the quantity of interest. In all cases the exposures were less than the critical energy for destruction and the cloth samples remained essentially intact. At the higher exposures, each yarn deteriorated with a considerable increase in optical transmittance of the fabric. Since one square centimeter of 9 oz yd^{-2} sateen weighs 0.03 g, the highest quantity of tar collected from untreated fabric, about 0.0025 g, amounts to about 8 percent of the initial fabric mass.

At low exposures, the amount of tar collected was rather small but at about $Q = 7.5$ cal cm^{-2}, the curves start to rise sharply. For the untreated fabric, the curve for the contact arrangement tends to level off at about 0.0012 g cm^{-2} and for the spaced arrangement, at about twice that value. The curve for the FR treated fabric in contact seems to follow a somewhat different course than for the untreated fabric; above $Q = 12$ cal^{-2}, much more tar is collected for the FR
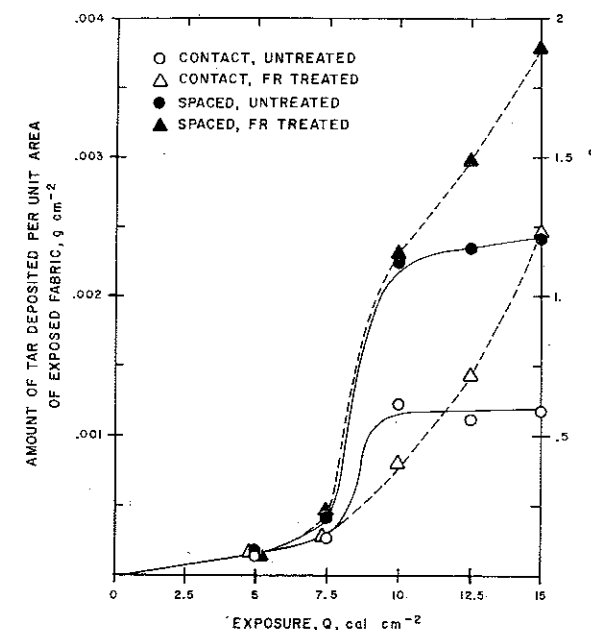

Fig. 2. Amount of tar deposited and estimated quantity of heat transferred to the skin for various exposures.

treated fabric. For the spaced condition, the two fabrics behaved somewhat similarly up to 10 cal cm^{-2}; above that, the FR fabric again produced much more tar than the untreated fabric.

Qualitatively, the results are understandable and seem reasonable. At the same exposure, fabrics spaced from the backing get much hotter than those in contact and suffer more deterioration. Possibly the increased amounts of tar from the treated fabric represent decomposition products of the BTAP and if so, the composition of the tars in the two cases is not the same. The add-on of BTAP changes the optical absorption and increases the heat capacity of the fabric. Very likely for the same exposure the temperature of the treated fabric is lower than that of the untreated fabric. At the same temperature, the amount of tar deposited and the amount of heat transferred for the FR treated fabric would likely be somewhat higher than for the untreated fabric, at all exposures. The leveling off of the curves for the untreated fabrics at $Q = 12.5$ to 15 cal/cm^2 is not readily understood.

Collection of Large Amounts of Tar

Large amounts of tar were produced using the collector shown in Figure 3. The fabric was stretched lightly across the end opening D, i.e., it was
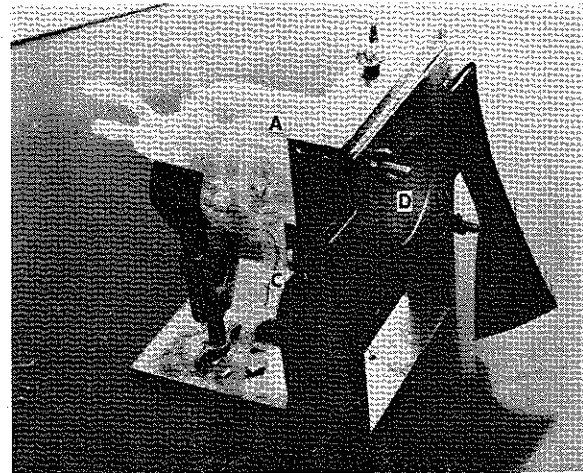
Fig. 3. Device for collecting large amount of tar. a. Cooled surface on which tar is collected. b. Water inlets and outlets. c. Tar outlet. d. Exposed fabric.

exposed with air backing. On exposure, the volatile products condensed on the water cooled walls and flowed down through a fiber glass filter into a vial surrounded by dry ice.

Two methods of irradiating the sample were used. In both, the fabric was in strips about 2 in. wide. In the first method, part of the sample was exposed to a single rectangular pulse of radiation, the strip was moved to a new area, and the process repeated until about 10 ml of tar was collected. The irradiance H was 10 cal cm^{-2} sec^{-1}, the exposure time 2 sec; the exposure Q, 20 cal/cm^{-2}. In the second method, the strip of fabric was moved across the opening at a constant rate, adjusted to give the desired exposure at any point. In this method the exposure was either 10 or 20 cal cm^{-2}.

Six samples of tars were produced, one by the single pulse method and three by the continuous method from untreated fabric, and two by the continuous method from FR treated fabric. These are listed in Table I.

Feldman [6] and Mixter and Krolak [20] have measured the critical exposure Q_c for destruction of fabric with an air backing. Feldman's result for 9 oz yd^{-2} OG-107 sateen, untreated, is 16.5 cal cm^{-2}. As expected from this value, the fabric for samples 1 and 2 was almost completely destroyed. For samples 3, 4, 5, and 6, the exposure was below the critical value and the fabric was not destroyed; it remained in place during the entire time of the exposure.

Enthalpy Change of Tars

The measurement of the enthalpy change of the tar is complicated by inhomogeneity of the material, incomplete evaporation and apparent decomposition of the material. This was evident from some preliminary experiments. At atmospheric pressure, there was considerable carbonization. The results of distillation at atmospheric pressure in a microstill, with a capacity of 4 ml, constructed according to the design of Javes, Liddell and Thomas [11] are shown in Figure 4. With an initial sample of 3 ml, about half evaporated at about 98° C and up to two-thirds at the maximum obtainable head temperature of 113° C. The distillate was recombined with the residue and reheated. As shown by the second curve, some material distilled at a slightly lower temperature, 96° C, as compared to 98° C, but only about half as much could be vaporized. The residue was black and viscous at high temperature and cooled to a porous coke-like mass.

In flash evaporation at atmospheric pressure from a hot surface, about half the sample evaporated at 100° C, another one-fourth at 200° C, and perhaps another one-twentieth at 300° C, leaving a black varnish-like residue. In vacuum distillation, over a pressure range of 0.1 to 2 microns, 56 percent of the material evaporated at 95° C, leaving an amber glassy residue.
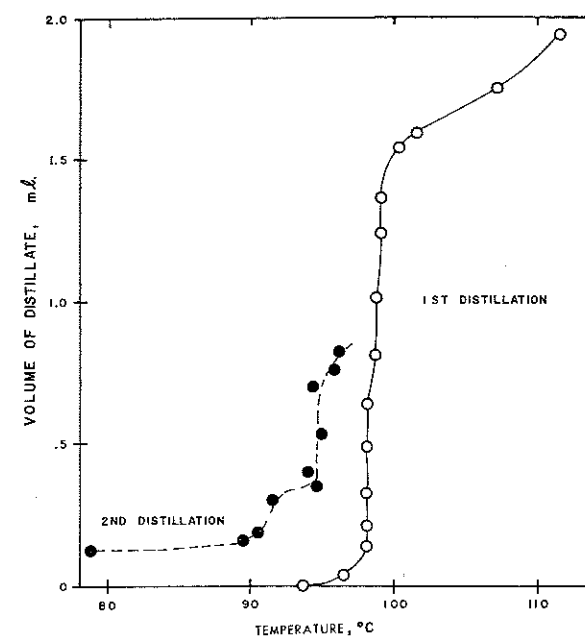

Fig. 4. Amount of tar re-distilled at various temperatures.

TABLE I. Enthalpy Change Estimated from Heat Transferred from Calorimeter to Tar

Sample	Fabric	Type	Exposure conditions time, seconds	Exposure conditions exposure Q, cal cm^{-2}	Calorimeter temperature, ° C run	Calorimeter temperature, ° C initial	Calorimeter temperature, ° C Final	Heat transferred, cal	Sample weight, g	Fraction vaporized	Enthalpy change, cal per g of tar evaporated Each run	Enthalpy change, cal per g of tar evaporated Av.
1	Untreated	Single	2	20	2	227.3	220.7	79.4	.1958	.755	512	
					3	179.4	172.1	88.4	.2342	.694	518	515
2	Untreated	Continuous	2	20	4	178.1	172.3	69.4	.2139	.667	457	
					13	173.8	164.5	112.5	.3163	.706	481	
					5	149.4	147.0	29.1	.0823	.640	526	488
3	Untreated	Continuous	1	10	10	179.7	172.2	88.7	.2070	.776	535	
					6	149.8	143.3	79.0	.1909	.738	544	540
4	Untreated	Continuous	1	10	11	180.3	173.6	81.9	.2145	.650	555	
					7	150.0	143.6	77.1	.2160	.630	539	547
												$\overline{522}$
5	FR	Continuous	2	20	8	150.0	144.4	67.3	.2231	.539	519	
					12	122.6	117.8	56.4	.2229	.461	505	512
6	FR	Continuous	2	20	9	150.1	143.2	82.4	.2308	.648	525	525
												$\overline{518}$

From these observations, the method selected for determining enthalpy changes was to add the cold material drop by drop, at atmospheric pressure, to a hot calorimeter of low heat capacity. The temperature change of the calorimeter and contents and the amount of material evaporated afford a measure of the enthalpy changes.

The calorimeter was of copper, $\frac{3}{4}$ in. in diameter and 2 in. long, with an upper axial well for the sample $\frac{3}{16}$ in. in diameter, extending from the top surface to about the middle, and a lower axial well, for a thermocouple, $\frac{1}{32}$ in. in diameter, extending from the bottom to within $\frac{1}{8}$ in. of the sample well. The device was made of two parts which could be unscrewed for cleaning. The components were gold plated. To heat the calorimeter, it was suspended in a 1 in. I.D. vertical furnace by two AWG 30 constantan wires. A single-junction AWG 30 copper constantan thermocouple was used to measure the temperature.

The sample, either tar or calibrating liquid, was dropped into the calorimeter from a 1 ml syringe clamped above the furnace. In most cases the needle was No. 26 with the tip ground square but for very viscous samples a No. 20 needle was used.

In use, the calorimeter was suspended in the preheated furnace. Alignment of the syringe was checked by observing water drops falling into the furnace. The syringe was removed, dried, weighed, filled with sample, reweighed and replaced. When the empty calorimeter reached the desired temperature, thermocouple readings were taken every 30 sec for 2 or 3 min to determine the foredrift. The sample was then added at the rate of about 1 drop per second.

Thermocouple emfs were again recorded at 30-sec intervals for four minutes. A typical temperature record is shown in Figure 5. The fore and after drift emf plots were arbitrarily extrapolated to 30 sec after the last foredrift readings; this time corresponded approximately to addition of half the sample. The difference between the two extrapolated curves at this time was taken as a measure of the temperature change of the calorimeter due to heat transferred to the sample.
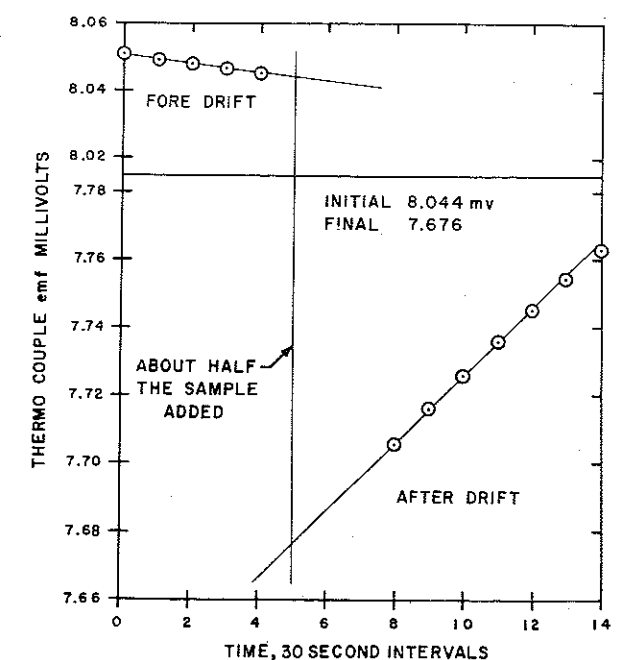

Fig. 5. Temperature changes in the calorimeter.

The syringe and the cooled calorimeter were weighed after the run. The changes in weights gave the total sample and the residue.

A combination of two methods was used to calibrate the calorimeter. In the first method, the heat capacity was estimated from the equation for pure copper as given by Bronson, Chisholm and Dockerty [2].

$$\text{Heat capacity} = M \left[0.09663 + 6.8 \times 10^{-6} \ (T_1 + T_2) - \frac{452}{(T_1+273)(T_2+273)} \right] \quad (1)$$

where M is the mass and T_1 and T_2 are the initial and final temperatures, in ° C, and the heat capacity is in cal ° C⁻¹.

In the second method, water was dropped into the calorimeter, which was near 100° C. The enthalpy change was calculated from

$$\text{Total enthalpy change} = m\,C_w\,(T_1 - T_2) + mV \quad (2)$$

where the temperatures are as above, m is the mass of the water, C_w is the average specific heat of water over this range, V is the heat of vaporization at the existing pressure.

Values for the heat capacity of the calorimeter, as determined with water, included contributions from the gold plate, supporting wires, and thermocouple under representative conditions of use, but were restricted to temperatures near 100° C. The first method, on the other hand, provided heat capacity values at any desired temperature for an idealized calorimeter of pure copper.

In a series of seven runs, the heat capacity by the water method was 0.32 cal ° C⁻¹ higher than by the first method. This difference was used as a constant correction to be added to the heat capacity of the calorimeter as calculated by Equation 1.

The average value of the heat capacity in the calibration runs was 11.83 cal ° C⁻¹. The standard deviation of the differences between the two calibration methods for these seven runs was 0.7 percent. This value is an indication of the precision with which the total enthalpy change of a sample could be measured by the calorimeter. For measurement of the tars, the standard deviation among duplicate runs on five specimens was 3 percent. The poorer reproducibility, as compared to the calibration runs, was probably due to spattering and incomplete evaporation of the tars.

With tar samples of 0.1 to 0.3 g, the temperature drop of the calorimeter was 3 to 9° C.

The results for one to three runs on each sample of tar are given in Table I, along with the method of producing the tar. Run 1 on sample 1 is not included; this result was very low probably because of excessive spattering.

The heat given by the calorimeter to the tar is distributed among several effects. The tar residue is heated from the initial temperature to the final calorimeter temperature. No measurements were made of the average specific heat of this material but comparison with materials of similar composition indicates the value is probably between 0.3 and 0.5 cal g⁻¹ ° C⁻¹. The tar evaporates over a range of temperatures, probably half at about 100° C and the rest between 100° C and the varying temperature of the calorimeter. Some heat is expended in heating the vapor above its evaporating temperature. This is probably small and has been neglected. The last column of Table I is the enthalpy change of the evaporated tar allowing for heating of the residue with an estimated average specific heat of 0.4, and expressed in cal/g of tar evaporated. The uncertainty of this procedure is not very great; changing the specific heat from 0.4 to 0.5 g⁻¹ ° C⁻¹ lowers the enthalpy change in the last column of Table I by about only 7 cal g⁻¹ or about 1.5 percent.

The origin of the residue in these experiments is of some concern. One possibility is that all the material is condensed vapor and that changes which occurred after collection account for the part which could not be re-evaporated. If this is the case, then the value of the enthalpy change in Table I probably represents fairly well the heat transferred by the tar in typical exposures. On the other hand, it may be that with high irradiance, the evaporation takes place in such an explosive manner that unevaporated material is carried over with the volatile material, i.e., some of the material collected, either by the method used here for collecting large amounts or in typical protection exposures, never existed as a vapor. In that case the values in Table I are much too high, perhaps by 25 to 35 percent for samples 1, 2, 3, and 4 and even more for samples 5 and 6. At present it seems that the first possibility is more likely.

Within the limits of these uncertainties, there does not seem to be a significant difference between the values for tars from the two different fabrics. Also,

there is little difference between the values for the different methods of producing tar.

The heat of vaporization accounts for the larger part of the enthalpy change. An approximate calculation was made assuming about half the sample was water and evaporated at 100° C and the rest was material having a specific heat of .4, evaporating at a somewhat higher temperature, about midway between 100° C and the final calorimeter temperature. The result indicates the effective heat of vaporization is about 463 cal g⁻¹, accounting for about 89% of the enthalpy change.

In a typical exposure, the sensible heat will be slightly lower than in the calorimeter. The temperature of the backing rises during the exposure with an average temperature perhaps 12° C higher than the initial temperature of the tar in the calorimeter. Likewise the initial tar temperature on production, although uncertain, is likely lower than final temperature in the calorimeter. An approximate calculation similar to that above shows that the difference is about 8 cal g⁻¹. In view of these uncertainties, for the present purpose, the effective enthalpy change was rounded off to 500 cal g⁻¹.

The results in Figure 2 and Table I showing about half the material evaporating at about 100° C would be expected from the chemical analysis indicated above. This analysis also provides a very approximate check on the heat capacity. The heat required to convert water at room temperature to steam at 100° C is about 615 cal g⁻¹ and to steam at 170° C is about 640 cal g⁻¹. Since organic liquids generally have lower heats of vaporization than water, a somewhat lower value would be expected from the tar.

Heat Transferred by the Tar

The heat transferred to the skin or skin simulant was evaluated by combining the results for the amount of tar in Figure 2, with the enthalpy change from Table I, i.e., 500 cal g⁻¹, with the result indicated by the scale on the right of Figure 2.

For exposures less than $Q = 5$ cal cm⁻², the amount of heat transferred by the tar is very small, no more than .1 cal cm⁻² of fabric. For the untreated fabric the maximum amounts are about .6 cal cm⁻² for contact and up to 1.2 cal cm⁻² spaced. For the FR treated fabric the corresponding maximum amounts at 15 cal cm⁻² are 1.2 and 2 cal cm⁻².

Contribution of Tars in Producing Skin Burns

The heat transferred to the calorimeter can be measured fairly accurately but difficulties in handling the sample increased the error slightly and other factors such as incomplete evaporation of the tar and uncertainty about the heat capacity of the liquid tar and the residue and the temperature at which it is produced in typical exposures increase the uncertainty in the application of these results. In spite of these factors and largely because a large fraction of the heat transferred is accounted for by the heat of vaporization, the results are fairly definite. Unfortunately, estimation of the effect of this heat transfer in producing skin burns is even more uncertain. Even so, some fairly definite conclusions can be drawn from an analysis which includes consideration of the rate of burning of skin, the relation between power input and the temperature rise of the skin, and data on the irradiation of blackened skin.

Rate of Burning of Skin

The burning of skin is a temperature dependent rate process. Henriques [8] has shown that this rate is given by

$$d\,\Omega/dt = 3.1 \times 10^{98}\, exp\,[-75,000/(T+273)] \quad (3)$$

where Ω is the degree of burn and T is the temperature of the skin in ° C. This is the usual Arrhenius relation but his value of 150,000 cal mol⁻¹ for the activation energy represents a very high temperature coefficient. In the range from 48 to 60° C, this corresponds to about doubling the rate for a 1° C rise in temperature.

These rates were based on a study of burns of human and pig skin, with the surface held at a more or less constant temperature. Observations were made of both surface and sub-surface appearance, largely the latter. A threshold was defined as the shortest time at a given temperature to produce irreversible transepidermal necrosis [9]; for this damage $\Omega = 1$. The coefficient in Equation (3) was determined from this value of Ω and the integrated value of the exponential term. The same temperature coefficient was assumed for less severe burns; in a few cases this was shown to be justified.

Moritz and Henriques [9] gave the location of the epidermis-dermis interface in pig skin as .008 cm below the surface. Pig skin is not homogeneous but the effective thermal conductivity is about .0015 cal cm⁻¹ sec⁻¹ ° C⁻¹; the density is about 1 g cm⁻³.

Grading of Burns Produced by Short Pulses of Thermal Radiation

In our laboratory, burns produced by intense thermal radiation, on bare or protected pig skin, are graded by a method similar to the above [24]. About 24 hours after exposure, the exposed area is pushed laterally with a blunt instrument. If the epidermis does not separate from the dermis, the severity is less than 2+, either 1+ if red, or 0 if there is no visual evidence of change. If the epidermis separates, the burn is at least 2+ in severity; if the underlying dermis is red, it is 2+, if it is gray, it is 3+. The criteria are summarized in Table II.

TABLE II. Criteria for Grading Pig Skin Burns at U. S. Army Natick Laboratories

Designation	Description
0	No detectable visual change in the surface.
1+	Surface red (erythema); the epidermis not readily separable from the dermis.
2+	Epidermis readily separable from the dermis by lateral pressure with a blunt instrument. Underlying dermis pink or red.
3+	Epidermis separable from the dermis as above but less readily than for 2+. Underlying dermis gray or white.
4+	Full thickness destruction of the dermis rendering it penetrable by a relatively blunt probe.

Generally in such exposures the irradiance is not uniform over the exposed area. The result is that the burn is not uniform and this allows finer grading within each designation, i.e., mild (M), intermediate (I) and severe (S), depending, for severe burns, on the relation between the area of the most severe burn and irradiated area. A 2+M burn is generally considered to be the minimum incapacitating injury and most attention is given to burns of this severity.

Our experience in this field is based directly on studies at the University of Rochester. For most of their work, the criteria was somewhat different; they depended mainly on surface appearance, for example, coagulation for 2+ and 3+ burns [23, 1, 10]. The severity grades for the two methods do not agree exactly; the difference is not great but it may be significant in some comparisons of results, as will be mentioned later.

Effect of Duration of Thermal Pulse in Producing Burns

Heat delivered to the surface of the skin is carried rapidly away to the underlying skin and flesh. Ac-

cordingly, the critical energy to produce a given burn is greater the slower the energy is delivered. This is shown in Table III for irradiation of blackened pig skin, both for rectangular pulses used in our laboratory [3] and for shaped pulses similar to those from nuclear weapons used by Mixter at the University of Rochester [16]. The critical energy is expressed as $EE50\ 2+M$, i.e., the effective exposure that will produce burns of at least 2+ severity in 50 percent of the trials. For the shaped pulse, the time is t_M, the time to reach the maximum irradiance.

TABLE III. Critical Enery for Burning of Blackened Pig Skin

Pulse duration, sec	$EE\ 50$ $2+\ M$ cal cm^{-2}
a. Rectangular pulse, U. S. Army Natick Laboratories	
$\frac{1}{2}$	1.01
2	1.18
10	1.81
b. Shaped pulse, University of Rochester Time is t_M, the time to reach maximum irradiance	
0.127	1.66
0.179	1.9
0.283	1.9
0.40	1.93
1.265	2.79
4.00	4.21

Similar increases in critical energy with lengthening exposure time are observed for bare skin [23, 17, 14] but the blackened skin results are emphasized here because the heat transfer conditions are similar for directly irradiated blackened skin and for untreated skin protected, for example, by clothing. Excepting absorption of direct radiation, in all the other mechanisms of energy transfer that may be involved in heating protected skin, the energy is absorbed at or near the surface of the skin, as it is for direct irradiation of blackened skin. Accordingly, results for the two conditions can be compared directly.

Relation Between Power Input and the Temperature Rise of the Skin

For protected skin, regardless of the shape of the incident irradiance pulse, the power to the skin shows a fairly sharp rise followed by a slower decay. The one case analyzed most thoroughly [5] was that of a

skin simulant protected by a single layer of opaque 9 oz yd^{-2} cotton sateen, spaced from the simulant, and exposed to a 1-sec rectangular pulse, irradiance H = 6.36 cal cm^{-2} sec^{-1}. In this case all the possible mechanisms of heat transfer, except direct transmission through the fabric, are involved. The power pulse to the skin started after a slight lag and reached a maximum soon after the irradiance stopped; it continued for a long time and was appreciable even after 30 sec but most of the energy was transmitted in the first 10 sec. The temperature rise lagged appreciably behind the power input, reached a broad maximum at about 6 seconds and decreased very slowly after that. There was no evidence of multiple power pulses but perhaps they would not be readily apparent with such a broad temperature pulse.

There is some general information about the rates of transmission of energy to protected skin by the various processes. Energy transferred directly to the skin produces its effect very rapidly; essentially the resulting temperature rise in the skin will occur during the exposure. Power radiated from the back surface of the protective layer to the skin will lag somewhat. Energy convected between the two surfaces will show a slightly greater lag. Energy by mass transfer will be as fast as or faster than by radiation. A direct comparison of temperature rise curves

with two different protective layers, one producing tars and the other not, would show these effects very clearly but such an experiment does not seem feasible now.

Critical Energies for Protected Skin

The critical energies for skin protected by a single layer of 9 oz yd^{-2} cotton sateen are given in Table IV. Some of the data were obtained by Mixter and co-workers, using the University of Rochester carbon arc [18, 17]; some in this laboratory, using both the Natick Laboratories high current carbon arc [22] and the Natick Laboratories solar furnace [7]. The $EE50\ 2+M$ for the case where the fabric is in contact with the skin is about 4 cal cm^{-2}; for the spaced arrangement the value is about 13 cal cm^{-2}.

These values can be related to the amount of the tar deposited and the heat transferred shown in Figure 2. For the contact arrangement, critical exposures of 4 cal cm^{-2} correspond to about 0.05 cal cm^{-2} transferred to the skin by tar, for either untreated or FR treated fabric. For the spaced case, the critical exposure of about 13 cal cm^{-2} for untreated fabric corresponds to about 1.2 cal cm^{-2} transferred to the skin. For the FR treated fabric, the value is a little higher, about 1.6 cal cm^{-2}.

TABLE IV. Critical Energy for Burning of Pig Skin Protected with a Single Layer of 9 oz yd^{-2} Cotton Sateen. Rectangular Pulse Radiation

Fabric	Radiation source	Exposure time, sec	$EE50\ 2+$, cal cm^{-2} Contact NLABS	Contact Rochester	Spaced Rochester 0.2 cm	Spaced Rochester 0.5 cm
OG-107 Untreated	Arc	$\frac{1}{4}$		4.9		
		$\frac{1}{2}$	3.7 3.2 4.3 3.5	5.1	9.9	
		1	3.1	5.5		
OG-107 Untreated	Solar furnace	$\frac{1}{2}$	4.3			
OG-107 FR treated	Arc	$\frac{1}{2}$	3.1	4.5	13.9	
Black Untreated	Arc	$\frac{1}{4}$	3.3			
		$\frac{1}{2}$	3.2			11.7
		1	3.5			15.0
		5	3.9			10.9

*Calculation of Temperature Rise in and Rate of
Burning of the Skin for Assumed Power Pulses*

In order to relate the heat transferred to the skin by the tars to the resulting burns, some calculations have been made for a few pulses which were assumed to represent the power input to the skin. For this purpose it was assumed that the power pulse p to the skin can be represented by

$$p = R\ t^{-3/2}\ exp\ (-r^2/4t)$$

where R and r are constants and t is the time. This pulse is of the correct general form in that p first increases rapidly and then decays more slowly, with a maximum p_M at a time $t_M = r^2/6$. This particular pulse was chosen, partly for this reason, and also because the temperature rise resulting from it can be calculated fairly easily. Other fairly simple forms are also available [5]. The exact shape of the pulse is not known; presumably it does not correspond to any simple form and at best can be represented by a combination of them. As will be evident later, variations in the shape of the pulse do not have much effect on the conclusions. At present the form chosen seems as good as any and has the advantage of simplicity.

For this input pulse, the temperature rise w is given by [5]

$$w = 2\ R\ \beta^{-\frac{1}{2}}\ r^{-1}\ t^{\frac{1}{2}}\ exp\ [-(r + x/\alpha^{\frac{1}{2}})^2/4t]\quad (5)$$

where β is the thermal inertia, $\beta = k\rho c$; α is the thermal diffusivity, $\alpha = k/\rho c$; k is the thermal conductivity, ρ is the density, c is the specific heat and x is the depth. The temperature rise also shows a maximum w_m at $t_m = (r + x/\alpha^{\frac{1}{2}})^2/2$. In deriving Equation 5, it is assumed that the skin is inert; it has been demonstrated that it is inert or nearly so [3].

The temperature was obtained from w by assuming the initial skin temperature to be 37° C. The rate of burning of the skin was determined using Equation 3 and the value of Ω was obtained by numerical integration, using Simpson's rule.

It was assumed that the power input to the skin, for 9 oz yd^{-2} fabric in contact with the skin, with an exposure of 4 cal cm^{-2}, producing a 2+M burn, is that labeled 1 in Figure 6. For this pulse, $R = 2.612$ cal cm^{-2} sec$^{-\frac{1}{2}}$ $r = 6^{\frac{1}{2}}$ sec$^{-\frac{1}{2}}$ and $t_M = 1.0$ sec. For thermal constants of the skin, $\beta^{\frac{1}{2}} = .0375$ cal cm^{-2} sec^{-1} and $x/\alpha^{\frac{1}{2}} = 0.213$ sec$^{\frac{1}{2}}$, the temperature rise w
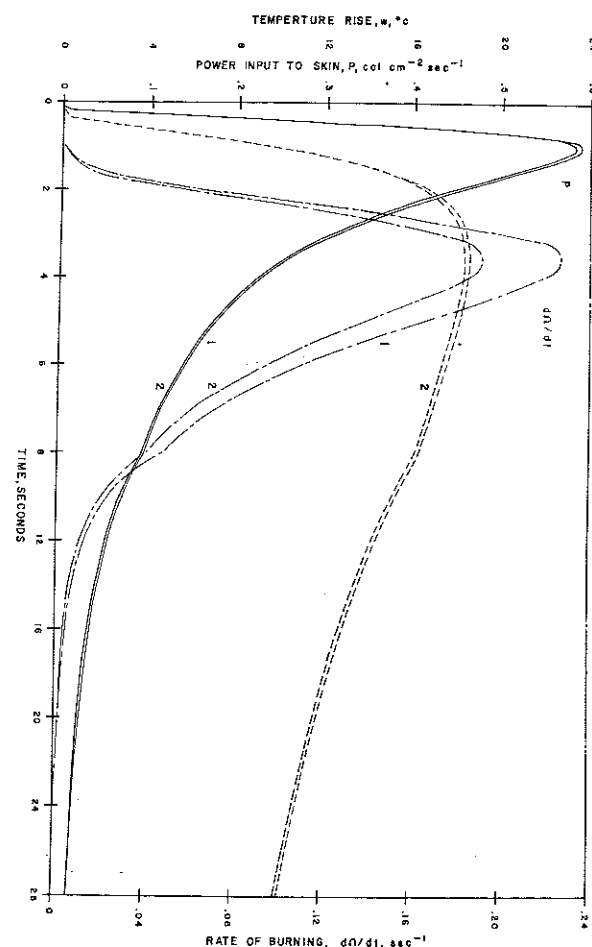

Fig. 6. Calculated temperature rise and rate of burning of skin for an input pulse assumed for the contact arrangement. $t_M = 1$ second; absorbed energies of 3.83 and 3.78 cal cm^{-2}.

is given by the corresponding curve labeled 1, with a maximum at $t_m = 3.54$ seconds. The rate of burning, $d\Omega/dt$ is given by the corresponding curve labeled 1. The value of R was chosen to make Ω about 1, actually 1.01; the total energy in the pulse is 3.83 cal cm^{-2}.

The temperature rise curve seems to be fairly reasonable for this condition but the energy in the pulse agrees only fairly well with the critical energy for blackened skin burns. The interpolated $EE50$ 2+M from Mixter's data in Table III is about 2.6 cal cm^{-2} for $t_M = 1$ second; allowing for a reflectance of about 0.05, the absorbed energy is about 2.5 cal cm^{-2}. Mixter's curve was cut off at about 10 t_M. The energy beyond t_M amounts to about 0.18 of the total and, for the case considered here, likely has only a small effect on the temperature rise or the burn.

The total energy in the full pulse would be about 2.5/.82 or 3.1 cal cm^{-2}, still somewhat less than 3.83 cal cm^{-2}.

The energy transferred by the tar as indicated in Figure 2 for this arrangement is about 0.05 cal cm^{-2} and without this energy would be 3.83 − .05 = 3.78 cal cm^{-2}. The curves labeled 2 in this figure represent p, w and $d\Omega/dt$ for this energy. The calculated value of Ω is 0.86. This reduction of 0.15 does not seem to be significant.

The curves labeled 1 in Figure 7 show the corresponding values for a pulse assumed to represent the critical power input to the skin for the spaced arrangement, i.e., $Q \simeq 13$ cal cm^{-2}. In this case, $R = 4.365$ cal cm^{-2} sec$^{-\frac{1}{2}}$, $r = 3.251$ sec$^{-\frac{1}{2}}$, $t_M = 1.762$ and $t_m = 6$ sec. The same skin constants were used as before. The total input energy to the skin was adjusted to 4.76 cal cm^{-2} to make $\Omega = 1.0$. The interpolated value of $EE50$ 2+M from Mixter's data in Table III is 3.1 cal cm^{-2}; again allowing for a reflectance of 0.05, the absorbed energy is 2.9 cal cm^{-2}, or for the full pulse 2.9/.82 = 3.5 cal cm^{-2}, considerably less than 4.76 cal cm^{-2}.

The energy transferred by the tars for the spaced condition for untreated fabric as indicated in Figure 2 is about 1.2 cal cm^{-2}. Reducing the input energy by this amount, i.e., by about 1.2/4.76 or about 1/4, to 3.56 cal cm^{-2}, gives the corresponding curves labeled 2. The temperature rise is correspondingly smaller and now the rate of burning is very small; the value of Ω is only about 0.05.

In the above calculation, there is the implicit assumption that the tar pulse has the same time constant as the combined pulse from all other effects. To determine whether this assumption affects the results appreciably, another calculation was made. The power input pulse to the skin was assumed to consist of two pulses having different time constants, the first corresponding to the tar contribution, with a total energy of 1.2 cal cm^{-2} and $t_M = 1.0$ sec, and the second with a total energy of 3.32 cal cm^{-2}, with $t_M = 1.76$ sec. This composite pulse produced a maximum temperature rise of 17.94° C with no readily observable evidence of two peaks. The corresponding value for the single pulse in Figure 7 is 17.73° C. The maximum rate of burning for this double pulse is .146 sec^{-1}, as compared to 0.127 sec^{-1} for the single pulse; both give values for Ω of about 1. The total energy in the double pulse is 4.52 cal cm^{-2}. Now on reducing the energy by the same amount as before,
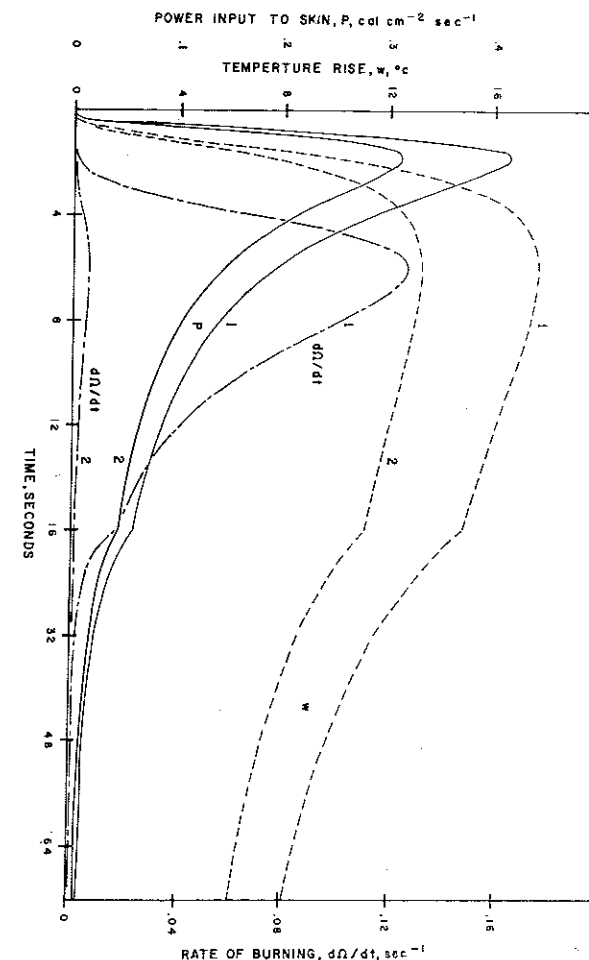

Fig. 7. Calculated temperature rise and rate of burning of skin for an input pulse assumed for the spaced arrangement. $t_M = 1.762$ seconds; absorbed energies of 4.76 and 3.56 cal cm^{-2}.

i.e., by 1.2 cal cm^{-2}, by eliminating the earlier of the two pulses, the maximum temperature rise w was reduced to 12.38° C and the maximum rate of burning, $d\Omega/dt$, to 0.0023 sec^{-1}. With an input energy of 3.32 cal cm^{-2}, the value of Ω is 0.03, not much different than for the single pulse in Figure 7.

Calculations have not been made for corresponding conditions for the FR treated fabric. Obviously, the results for contact would be similar and for the spaced arrangement, the effect of the tars would be even greater.

For the pulses in Figures 6 and 7, the total energy was considerably greater than the experimental results of Mixter. A sharper pulse, i.e., a faster rise and a faster decay, would in general reduce the energy corresponding to a given Ω and give better agreement.

Also, the $2+M$ burn as evaluated by him may correspond to a value of Ω somewhat less than 1 and this would reduce the calculated energy. The disagreements are probably not significant in estimating the contribution from the tars. The method used here involves determining the difference in effects between two pulses; in the process of taking the difference, the influence of pulse shape tends to cancel. The comparison of the effects of single and double pulses show that pulse shape is not very important in this determination. Many of the factors involved in this analysis are known very well in a qualitative way. Expressed quantitatively, the information becomes rather approximate. With the present state of knowledge, it is scarcely worth while to look for pulse shapes that will give better agreement. This is especially true since the results are so striking, i.e., a very small contribution from the tars for the contact arrangement and a very large contribution from the tars for the spaced arrangement. Possibly the former effect could have been anticipated without the benefit of calculations; the latter effect is not so obvious.

Conclusions

Quite large amounts of heat may be transferred to the skin by condensable decomposition products from cotton fabrics. The amount is about 500 cal g^{-1} of tar; most of this amount represents heat of vaporization. The amount of heat transferred in typical exposures depends on the arrangement of the protective layer. For a single layer of 9 oz yd^{-1} cotton, in contact with the skin, the amount is about 0.05 cal cm^{-2} of fabric at the critical exposure for producing disabling burns, for both untreated and FR treated fabric. Spaced from the skin, the corresponding energies are about 1.2 cal cm^{-2} for untreated and 1.6 cal cm^{-2} for FR treated fabric.

In the attempt to estimate the significance of these amounts of energy in contributing toward the burns, by calculating the temperature history and the rate of burning of the skin for assumed power input pulses to the skin, difficulties occur because of several uncertainties. These are principally in the thermal constants of the skin, the activation energy for burning of the skin and the calculated values corresponding to the experimentally measured burns. Even with these uncertainties, the results are rather definite. For untreated fabric and for fabric treated with brominated triallyl phosphate, the contribution of the tars is very small for the contact agreement, i.e., most

of the energy transferred from hot fabric to skin is by other mechanisms. For the spaced arrangement, the heat transferred by the tars is significant, amounting to possibly one-fourth of the total energy causing the burns for untreated fabric and probably slightly more for the FR treated fabric. For the latter case, without these amounts of energy, the degree of the burn is greatly reduced.

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